



1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100 101 102 103 104 105 106 107 108 109 110 111 112 113 114 115 116 117 118 119 120 121 122 123 124 125 126 127 128 129 130 131 132 133 134 135 136 137 138 139 140 141 142 143 144 145 146 147 148 149 150 151 152 153 154 155 156 157 158 159 160 161 162 163 164 165 166 167 168 169 170 171 172 173 174 175 176 177 178 179 180 181 182 183 184 185 186 187 188 189 190 191 192 193 194 195 196 197 198 199 200 201 202 203 204 205 206 207 208 209 210 211 212 213 214 215 216 217 218 219 220 221 222 223 224 225 226 227 228 229 230 231 232 233 234 235 236 237 238 239 240 241 242 243 244 245 246 247 248 249 250 251 252 253 254 255 256 257 258 259 260 261 262 263 264 265 266 267 268 269 270 271 272 273 274 275 276 277 278 279 280 281 282 283 284 285 286 287 288 289 290 291 292 293 294 295 296 297 298 299 300 301 302 303 304 305 306 307 308 309 310 311 312 313 314 315 316 317 318 319 320 321 322 323 324 325 326 327 328 329 330 331 332 333 334 335 336 337 338 339 340 341 342 343 344 345 346 347 348 349 350 351 352 353 354 355 356 357 358 359 360 361 362 363 364 365 366 367 368 369 370 371 372 373 374 375 376 377 378 379 380 381 382 383 384 385 386 387 388 389 390 391 392 393 394 395 396 397 398 399 400 401 402 403 404 405 406 407 408 409 410 411 412 413 414 415 416 417 418 419 420 421 422 423 424 425 426 427 428 429 430 431 432 433 434 435 436 437 438 439 440 441 442 443 444 445 446 447 448 449 450 451 452 453 454 455 456 457 458 459 460 461 462 463 464 465 466 467 468 469 470 471 472 473 474 475 476 477 478 479 480 481 482 483 484 485 486 487 488 489 490 491 492 493 494 495 496 497 498 499 500 501 502 503 504 505 506 507 508 509 510 511 512 513 514 515 516 517 518 519 520 521 522 523 524 525 526 527 528 529 530 531 532 533 534 535 536 537 538 539 540 541 542 543 544 545 546 547 548 549 550 551 552 553 554 555 556 557 558 559 560 561 562 563 564 565 566 567 568 569 570 571 572 573 574 575 576 577 578 579 580 581 582 583 584 585 586 587 588 589 590 591 592 593 594 595 596 597 598 599 600 601 602 603 604 605 606 607 608 609 610 611 612 613 614 615 616 617 618 619 620 621 622 623 624 625 626 627 628 629 630 631 632 633 634 635 636 637 638 639 640 641 642 643 644 645 646 647 648 649 650 651 652 653 654 655 656 657 658 659 660 661 662 663 664 665 666 667 668 669 670 671 672 673 674 675 676 677 678 679 680 681 682 683 684 685 686 687 688 689 690 691 692 693 694 695 696 697 698 699 700 701 702 703 704 705 706 707 708 709 710 711 712 713 714 715 716 717 718 719 720 721 722 723 724 725 726 727 728 729 730 731 732 733 734 735 736 737 738 739 740 741 742 743 744 745 746 747 748 749 750 751 752 753 754 755 756 757 758 759 760 761 762 763 764 765 766 767 768 769 770 771 772 773 774 775 776 777 778 779 780 781 782 783 784 785 786 787 788 789 790 791 792 793 794 795 796 797 798 799 800 801 802 803 804 805 806 807 808 809 810 811 812 813 814 815 816 817 818 819 820 821 822 823 824 825 826 827 828 829 830 831 832 833 834 835 836 837 838 839 840 841 842 843 844 845 846 847 848 849 850 851 852 853 854 855 856 857 858 859 860 861 862 863 864 865 866 867 868 869 870 871 872 873 874 875 876 877 878 879 880 881 882 883 884 885 886 887 888 889 890 891 892 893 894 895 896 897 898 899 900 901 902 903 904 905 906 907 908 909 910 911 912 913 914 915 916 917 918 919 920 921 922 923 924 925 926 927 928 929 930 931 932 933 934 935 936 937 938 939 940 941 942 943 944 945 946 947 948 949 950 951 952 953 954 955 956 957 958 959 960 961 962 963 964 965 966 967 968 969 970 971 972 973 974 975 976 977 978 979 980 981 982 983 984 985 986 987 988 989 990 991 992 993 994 995 996 997 998 999 1000 1001 1002 1003 1004 1005 1006 1007 1008 1009 1010 1011 1012 1013 1014 1015 1016 1017 1018 1019 1020 1021 1022 1023 1024 1025 1026 1027 1028 1029 1030 1031 1032 1033 1034 1035 1036 1037 1038 1039 1040 1

PCT

(10) International Publication Number
WO 01/66627 A1

POMEROY, John, E., III; P.O. Box 256, Grapeville, PA 15634 (US). **PETERSON, Kristen, M.**; Apartment 23B, 49 Rosewood Court, Pittsburgh, PA 15236 (US). **PAYNE, Peter, F.**; 126 Longview Drive, Irwin, PA 15642 (US).

(22) International Filing Date: 24 January 2001 (24.01.2001)

(74) Agents: RYWALSKI, Robert, E.; Omnova Solutions Inc., 175 Ghent Road, Fairlawn, OH 44333 et al. (US).

(25) Filing Language: English

(81) Designated State (national): JP.

(26) Publication Language: English

(84) Designated States (regional): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).

(30) Priority Data:
09/521,457 8 March 2000 (08.03.2000) US

(71) Applicant: OMNOVA SOLUTIONS INC. [US/US]; 175 Ghent Road, Fairlawn, OH 44333 (US).

Published:
— *with international search report*

(72) Inventors: KAUSCH, Charles; 4312 Cobblestone Drive, Copley, OH 44321 (US). VERROCCHI, Anthony; Apartment C-10, 2888 Mogadore Road, Akron, OH 44305 (US).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Year	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041	2042	2043	2044	2045	2046	2047	2048	2049	2050	2051	2052	2053	2054	2055	2056	2057	2058	2059	2060	2061	2062	2063	2064	2065	2066	2067	2068	2069	2070	2071	2072	2073	2074	2075	2076	2077	2078	2079	2080	2081	2082	2083	2084	2085	2086	2087	2088	2089	2090	2091	2092	2093	2094	2095	2096	2097	2098	2099	2100
1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041	2042	2043	2044	2045	2046	2047	2048	2049	2050	2051	2052	2053	2054	2055	2056	2057	2058	2059	2060	2061	2062	2063	2064	2065	2066	2067	2068	2069	2070	2071	2072	2073	2074	2075	2076	2077	2078	2079	2080	2081	2082	2083	2084	2085	2086	2087	2088	2089	2090	2091	2092	2093	2094	2095	2096	2097	2098	2099	2100	

WO 01/66627 A1

(54) Title: FLAME RESISTANT POLYOLEFIN COMPOSITIONS CONTAINING ORGANICALLY MODIFIED CLAY

(57) Abstract: Nanocomposite compositions comprising organically modified clays and polyolefins or copolymers containing repeat units derived from olefins have flame retardant or flame resistant properties. Sheets and laminates of the nanocomposite can be utilized wherever flame retardant properties are desired.

BEST AVAILABLE COPY

FLAME RESISTANT POLYOLEFIN COMPOSITIONS CONTAINING ORGANICALLY MODIFIED CLAY

5

FIELD OF INVENTION

The present invention relates to a nanocomposite composition, comprising polyolefins and organically modified clay, which exhibits flame retardant and flame resistant properties. The composition can be formed into a sheet or film. The sheet can further be utilized in a multi-layer laminate. Both sheets and laminates are flame retardant and are suitable for use as roofing membranes and protective coverings.

15

BACKGROUND OF THE INVENTION

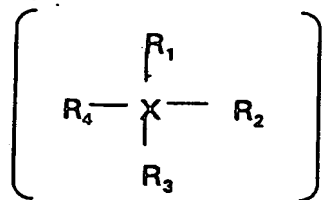
Traditional flame retardants include numerous halogenated organic compounds which extinguish the ignition (flame) source and inhibit chemical decomposition in the flame and inorganic materials such as aluminum trihydrate which release volatiles such as water which cause the flame to extinguish.

U.S. Patent No. 4,317,737 relates to polyolefin lubricant base oils which can be gelled by layer and chain type overtreated higher dialkyl dimethyl ammonium clays preferably containing a minimum of 12% excess of the quaternary ion moiety over their ion exchange capacity. For example, an overtreated dihydrogenated ditallow ammonium montmorillonite containing a 22% excess of the quaternary ion can be used to prepare a polydecene based grease although it does not gel mineral oil lubricants.

U.S. Patent No. 4,434,075 relates to an organophilic clay gellant which comprises the reaction product of an organic cation compound, an organic anion, and a smectite-type clay having a cation exchange capacity of at least 75 milliequivalents per 100 grams of said clay. The organic cation compound has the formula:

35

5



10

15

wherein R_1 is selected from the group consisting of a $\beta\gamma$ unsaturated alkyl group and a hydroxyalkyl group having 2 to 6 carbon atoms and mixtures thereof; R_2 is a long chain alkyl group having 12 to 60 carbon atoms; R_3 and R_4 are individually selected from the group consisting of a $\beta\gamma$ unsaturated alkyl group, a hydroxyalkyl group having 2 to 6 carbon atoms, an aralkyl group, an alkyl group having from 1 to 22 carbon atoms and mixtures thereof; X is selected from a group consisting of phosphorous and nitrogen. The reaction is carried out in a manner such that an organic cation-organic anion complex is intercalated with the smectite-type clay and the cation exchange sites of the smectite-type clay are substituted with the organic cation.

20

U.S. Patent No. 4,582,866 relates to flame retardant thermoplastic multi-block copolyester elastomer compositions containing a bromine-containing flame retardant; antimony trioxide; and an organophilic clay which is the reaction product of at least one quaternary ammonium salt with a smectite clay.

25

30

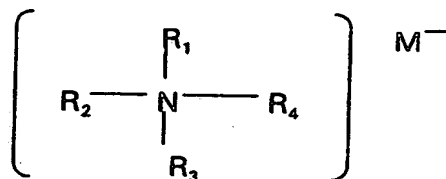
U.S. Patent No. 4,683,259 relates to resin-containing compositions, e.g. unsaturated polyester or epoxy resin compositions, are prepared using an organoclay of improved dispersibility. The organoclay is prepared by suspending a smectite clay in water to form a fluid suspension; treating the suspension with a solution of an inorganic salt, the cation of which has a valency of at least two, the concentration of the salt being such as to flocculate the smectite clay substantially completely; mixing the suspension of the flocculated smectite clay with a quaternary ammonium compound, at least one of

the four alkyl groups of which has from 10 to 24 carbon atoms; and dewatering the resultant product.

U.S. Patent No. 5,475,041 relates to a flame retardant composition which is provided comprising a normally flammable polyolefin or olefin copolymer, and a flame retardant amount of
 5 melamine or salt thereof, a polyphenylene oxide and a siliceous material.

U.S. Patent No. 5,718,841 relates to an organophilic clay comprising the reaction product of:

- 10 (a) a smectite-type clay; and
 (b) a quaternary ammonium compound or compounds selected from the group consisting of:



20 wherein R_1 is an unsaturated alkyl-ester group having 8 to 30 carbon atoms as described below and R_2 , R_3 and R_4 are independently selected from the group consisting of (i) R_1 ; (ii) long chain linear or branched alkyl (including methyl). Aliphatic or aromatic groups having 1 to 30 carbon atoms (such groups can also include hydroxylated groups); (iii)
 25 aralkyl groups, which are benzyl and substituted benzyl moieties, including such groups having fused ring moieties having linear chains or branches of 1 to 30 carbon atoms; (iv) aryl groups such as phenyl and substituted phenyl including fused ring aromatic substituents; (v) beta, gamma unsaturated groups having six or less carbon atoms or
 30 hydroxyalkyl groups having 2 to 6 carbon atoms; and (vi) hydrogen; and M is an anion selected from the group consisting of chloride, methylsulfate, acetate, iodide and bromide.

U.S. Patent No. 5,728,764 relates to organoclay compositions which comprise the reaction product of a smectite-type clay having an ion exchange capacity of at least 50 meq. wt. per 100 g. clay (active basis), and an alkoxylated quaternary ammonium compound having one or two alkoxylated chains containing 0-10 moles ethylene oxide and 3-15 moles of propylene or butylene oxide residues are useful thixotropic materials, especially for the preparation of aqueous systems.

U.S. Patent No. 5,773,502 relates to a flame retardant composition comprising: (a) a thermoplastic polyester and copolyester material, a halogenated organic fire retardant, antimony oxide, organo clay, and a fluorocarbon polymer. Also provided are compositions comprising glass fibers and stabilizers.

SUMMARY OF THE INVENTION

Organically modified clays are distinguished from halogenated flame retardants in that the clays generally form a nanometer scale composite when mixed with polyolefins, which exhibit enhanced fire retardant properties. The resulting nanocomposites do not sag or drip when exposed to a flame source, but hold their shape and inhibit flame spreading. The nanocomposite compositions can be formed into a sheet or laminate and are suitable for numerous applications including roofing membranes.

DETAILED DESCRIPTION

Titles have been provided in this application solely for illustration and do not limit the scope of the invention in any manner.

The compositions of the present invention comprise a polyolefin material integrated with microscopic or nanosize particles of

an organoclay material, which form a nanocomposite having enhanced flame retardant or resistant properties when compared to utilizing polyolefins alone. As used herein, nanocomposite is generally defined as substantially randomly dispersed particles of nanosized organoclay particles in a continuous polymeric (i.e. polyolefin) matrix.

The nanocomposites of the present invention should not be confused with ordinary compositions containing unmodified clay, i.e. natural clay and a polymer where the clay simply acts as a non-reinforcing filler, and has negligible impact on physical properties. However, the flame retardant compositions of the present invention can contain other components which also react or interact with the polymer as on a nanoscale level. The flame retardant compositions of the present invention are preferably melt processed.

POLYOLEFINS

The polyolefins utilized in the present invention are thermoplastic polymers or rubbers derived from one or more simple olefins, which have a total of from 2 to about 8 carbon atoms, or copolymers containing repeat units derived from an olefin. Carboxylic acid functionalized polyolefin polymers or copolymers can also be utilized containing up to about 8 percent by weight and preferably from about 1 percent by weight to about 5 percent by weight of the acid wherein the unsaturated acid contains a total of from 2 to about 10 carbon atoms such as acrylic acid, maleic acid, etc., or anhydrides thereof. Examples of polyolefins suitable for the present invention include polyethylene (including low-density, high-density, high molecular weight, ultra-high molecular weight, linear-low-density, very-low density, etc.), maleated polypropylene, polypropylene, polybutylene, polyhexalene, polyoctene, and copolymers, combinations or blends thereof. Examples of copolymers containing repeat units

derived from olefins include but are not limited to ethylene-vinyl-acetate (EVA) copolymers.

Preferred polyolefins or copolymers include polyethylene, maleated polypropylene, maleated polyethylene, polypropylene, EVA, copolymers of ethylene and octene, and ethylene-propylene rubber, that is, copolymers of ethylene and propylene. The ethylene propylene rubber that is utilized in the present invention generally contains from about 10 to about 90 weight percent ethylene and from about 90 to about 10 weight percent propylene, and desirably from about 15 to about 85 weight percent ethylene and about 85 to about 15 weight percent propylene. The ethylene and octene copolymer utilized in the present invention generally contains from about 10 to about 90 weight percent ethylene and from about 90 to about 10 weight percent octene, desirably from about 20 to about 80 weight percent ethylene and from about 80 to about 20 percent octene, and preferably from about 30 to about 70 weight percent ethylene and from about 70 to about 30 weight percent octene.

ORGANICALLY MODIFIED CLAY

In the present invention, it is desirable to use an organically modified clay, or organoclay which will form a nanocomposite with the polyolefin. The organically modified clays are generally prepared by reacting a clay with an organic cation or cations provided by specific quaternary ammonium compounds. The polyolefin and organoclay are intimately mixed and dispersed on a microscopic or nanoscale level resulting in a composition having increased heat and flame resistance. The organo clays of the present invention generally have a particle size from about 1 to about 10,000 nanometers, desirably from about 100 to about 2,000 nanometers, and preferably from about 200 to about 500 or 1,000 nanometers.

The organoclays of the present invention at least differ from ordinary untreated clays in the fact that the untreated clays typically form only ordinary phase-separated mixtures when blended or mixed with a polymer. The clays which are organically modified are more easily dispersed in the polymer matrix and can form a nanocomposite of two types: i.e. intercalated or exfoliated structures. It is preferable to utilize a clay with an exfoliated structure. Intercalated nanocomposites have polymer chains which are intercalated between the silicate layers of the clay resulting in a well ordered multilayer, where the layers of the clay retain their structural registry. Exfoliated nanocomposites are those in which the silicate clay layers or platelets having thickness on a nanometer scale, are exfoliated or separated, i.e. mechanically, by shear mixing, and are randomly and highly dispersed throughout the continuous polymer matrix. It is also possible that nanocomposites can be a mixture having both intercalated and exfoliated structures.

In order to obtain better compatibility between the polyolefin and organoclay, it is desirable that the organoclay contains substituted alkyl side chains.

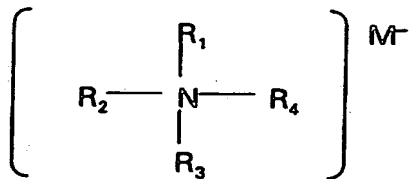
The types of clay minerals which can be utilized include, but are not limited to, smectite, vermiculite, halloysite, or any synthetic analogs or combinations thereof, with smectite-type clay being preferred. Smectite-type clays which are useful in preparing the required organoclays include montmorillonite, hectorite, bentonite, beidellite, stevensite, saponite, nontronite, sauconite, sobokite, and svinfordite.

The preferred clays used to prepare the organophilic clay of this invention are cation-exchangeable smectite clays which have the cation exchange capacity of at least 75 miliequivalents per 100 grams of clay, 100 percent active basis (i.e. beneficiated and essentially free

of non-clay impurities). Smectite-type clays are well known in science, geology and in the art of rheological additives, and are commercially available from a variety of sources both in the United States and throughout the world. They are unique among clays in that they exhibit the phenomena of swelling to many times their size when contacted with water.

The organic cations which can be reacted with a clay to form the organically modified clay utilized in the present invention and can be selected from a variety of nitrogen-based quaternary materials that are capable of exchanging cations with the selected smectite-type clay. The organic cations which are reacted with the smectite-type clay to prepare the inventive organophilic clays have a positive charge localized on a single nitrogen atom within the compound.

For this invention, the organic cation is provided by specific quaternary ammonium compounds derived in whole or in part from organic acid-derived esters. This organic cation is provided by a quaternary ammonium compound selected from the group consisting of the following formula:



wherein R_1 is an alkyl or aralkyl-ester group having 8 to 30 carbon atoms as described below and R_2 , R_3 , and R_4 are, independently, selected from groups such as (i) R_1 ; (ii) linear or branched alkyl (including methyl), aliphatic, or aromatic groups having 1 to 30 carbon atoms (such groups can also include hydroxylaryl groups); (iii) aralkyl groups, such as benzyl and substituted benzyl moieties, including such groups having fused ring moieties having linear chains or branches of 1 to 30 carbon atoms; (iv) aryl groups such as phenyl and substituted

phenyl including fused ring aromatic substituents; (v) beta, gamma-unsaturated groups having six or less carbon atoms or hydroxyalkyl groups having 2 to 6 carbon atoms; and (vi) hydrogen; M is an anion, typically chloride, methyl sulfate, acetate, iodide, and bromide. A further detailed description of organoclay compositions which are suitable for use in the present invention can be found in U.S. Patent No. 5,718,841 and 4,434,075 which are fully incorporated herein by reference.

Suitable organoclays for use in the present invention are available from Southern Clay Products, of Gonzales, Texas, under the trademark Cloisite 15A, Cloisite 20A, and SCPX - 1967, from Nanocor, Inc. of Arlington Heights, IL, tradename Nano #405, and from Rheox, Inc. (Elementis Specialties) of Hightstown, NJ, available as Rheox EA108, EA2827, EA2885, EA2886. Preferred organoclays are available from Rheox as EA2827 and EA2886.

The amount of organoclay utilized in the present invention generally is from about 2 to about 20 parts by weight, desirably, is from about 3 to about 15 parts by weight, and preferably is from about 4 to about 10 parts by weight per 100 parts by weight of polyolefin or polyolefin copolymers.

OTHER FLAME RETARDANTS

While the nanocomposite comprising a polyolefin polymer or copolymer and an organoclay has flame resistant or retardant properties and also does not sag or drip into a flame, thereby inhibiting it, the optional addition of other flame retardants to the composition can further enhance the performance of the nanocomposite compositions.

Flame retardants which can be utilized in the present invention include inorganic flame retardants such as but not limited to aluminum trihydroxide, magnesium oxide, magnesium hydroxide,

alumina trihydrate, ammonium polyphosphide, antimony oxide, antimony trioxide, barium borate, calcium sulfate dihydrate, diammonium phosphate, magnesium carbonate, or borate based compounds, or combinations thereof. Preferred inorganic flame retardants of the present invention are magnesium hydroxide, alumina trihydrate and antimony oxide. The inorganic flame retardants of the present invention can be used in an amount generally from about 0 or 0.1 to about 50 parts by weight, desirably from about 1, 5, or 10 to about 35 parts, and preferably from about 15 to about 25 or 30 parts by weight per 100 parts by weight of polyolefin polymer or copolymer.

The present invention is substantially free of polar organic and/or halogenated organic flame retardants. That is, the present invention comprises generally less than 10 parts, desirably less than 5, 3, or 1 parts by weight per 100 parts by weight of polyolefins and preferably is completely free of polar organic and/or halogenated organic flame retardants. Examples include but are not limited to triphenyl phosphate, halogenated organic phosphate, chlorinated polyphosphate, chlorinated organic phosphate, chlorinated paraffin, brominated organics, and chlorinated organics. It is preferable to minimize use of halogenated flame retardants because when exposed to flame or ignition source, they tend to give off or emit toxic or noxious gases such as HCl gas or HBr gas which are also not environmentally friendly. Polar organic compounds are avoided because they have low weatherability, have poor process ability and tend to stick to processing rolls, and give off toxic gases when burned.

ADDITIVES

In addition to the above noted components, the present invention can contain various amounts of conventional processing aids, additives or ingredients. Such compounds include UV inhibitors, release

agents, pigments such as carbon black and titanium dioxide, stabilizers, such as hindered phenols, antiozonates, phosphite and sulfides, and antioxidants. This list is merely an example of the potential additives and is by no means exhaustive. Such additives of the present invention
5 can be used in effective amounts to achieve desired properties.

NANOCOMPOSITE PREPARATION

Any method which provides uniform mixing or dispersion
10 between the organoclay with the polyolefin on a nanoscale or microscopic level can be used to prepare the compositions of this invention. Mechanical shearing methods can be employed such as single or twin screw extrusion, injection molding, Banbury type mixing, two-roll milling and the like. Shearing also can be achieved by
15 introducing the polymer melt at one end of an extruder (single or double screw) and receiving the sheared polymer at the other end of the extruder. The temperature of the polymer melt, the length of the extruder, residence time of the melt in the extruder and the design of the extruder (single screw, twin screw, number of flights per unit
20 length, channel depth, flight clearance, mixing zone, etc.) are several variables which control the amount of shear to be applied. It is important that the organoclays and polyolefins form a nanocomposite structure in order that the fire resistant or retardant properties of the compositions are maximized.

25 Preferably, the compositions of the present invention are processed into a sheet, film, membrane, or the like, or also formed into a multi-ply laminate or membrane.

A desirable method for forming sheeted compositions of the present invention is as follows: desired amounts of raw materials
30 including the organoclay and polyolefins of the present invention are

placed in a Banbury type mixer where they are mixed. The drop temperature of the Banbury is about 375°F. Generally, the temperature of the compound is from about 400 to about 440°F, and the mixing lasts for approximately 2 minutes and 20 seconds. The mixture is then transferred to two-roll mill, where the composition is milled and then further transferred to an extruder. The mixture is extruded through a die which preferably forms a rope or string-like extrudate, which can be put on a conveyor belt and transferred to a calender. The extrudate is then calendered to form the finished sheet material which generally has a thickness of from about 6 mils to about 50 mils, and preferably from about 18 mils to about 26 mils. Optionally, after the calendering step a backing and/or other layer or layers can be added or laminated to the flame retardant sheet thus forming a flame retardant laminate.

Another preferred method for preparing sheeted compositions of the present invention is as follows: the desired amounts of raw materials of the present invention are fed, preferably gravimetrically into an extruder, preferably a twin screw extruder and die extruded into a sheet or film. Optionally, the extrudate from the twin screw extruder can further be fed into a single extruder before being die formed into a sheet or film. The flame retardant sheet can be laminated with a backing, other layer or layers to form a flame retardant laminate.

LAMINATES

A further desirable embodiment of the present invention includes forming a laminate including at least one flame retardant sheet of the present invention. While not being limited thereto, a three layer laminate is preferred. The flame retardant laminate generally comprises a top layer comprising a flame retardant sheet of the present invention, a middle layer generally comprises a reinforcing backing such as a

woven or nonwoven polymer fabric layer such as polyester, nylon, etc., and a bottom layer which can be any suitable polymer layer such as but not limited to polyolefin polymers or copolymers as defined above, or a polyvinyl chloride layer. The laminates can be formed comprising at least one layer of the above noted flame retardant layer, a backing layer and a bottom or base layer as known by one of ordinary skill in the art. Generally, thicknesses of the at least three layer laminates range from about 20 to about 100 mils, desirably from about 30 to about 90 mils, and preferably from about 40 to about 70 mils.

The flame retardant sheets, laminates or membranes prepared from and according to the present invention are suitable for use where flame retardant properties are needed. Examples of suitable uses include but are not limited to films, laminates, wallcoverings, tents, tarps, and roofing membranes.

The National Highway Traffic Safety Administration standard, MVSS-302, specifies burn resistance standards for materials used in the occupant compartment of motor vehicles in order to reduce deaths and injuries to motor vehicle occupants caused by vehicle fires, especially those originating in the interior of the vehicle from sources such as matches or cigarettes. The MVSS-302 Standard states that a material "shall not burn, nor transmit a flame front across its surface, at a rate of more than 4 inches per minute." The flame retardant sheets or films prepared for the present invention have burn rates generally less than 4 inches per minute, desirably less than 3.5 inches, or less than 3.0 inches per minute and preferably less than 2.5 inches per minute when tested according to MVSS-302. As can be seen by the following examples, the flame retardant membranes of the present invention offer excellent flame retardant and flame resistant properties, and can be extremely beneficial when employed in any of the above stated uses.

The present invention will be better understood by

reference to the following examples, which serve to illustrate, but not limit the present invention.

EXAMPLES

5 The following examples were prepared on a laboratory two-roll hot mill. The temperature of the rolls was approximately 300-350°F. The order of the raw materials is dependent upon the composition of the formulation. Generally, the base polyolefin was added first, followed by the nanocomposite clay, flame retardant (ATH),
10 filler (Aluminum Silicate), color pigment, UV stabilizer, and antioxidant. After sufficient heat fluxing, the compound was sheeted off the mill at the desired thickness and tested according to MVSS-302 test parameters. All components are listed in parts by weight.

15 MVSS-302 TEST.

 The samples of this test are tested in accordance with The National Highway Traffic Safety Administration's MVSS Standard Number 302 for the flammability of interior materials, and a summary
20 of the test procedure is stated below.

 A 4 inch wide by 14 inch long sample is inserted into a U-shaped horizontal test fixture. A flame source such as methane or natural gas, typically a Bunsen burner, is applied to the sample so that the flame is 3/4 inch below the center of the bottom edge of the open
25 end of the specimen. The sample is allowed to burn until the flame reaches 1-1/2 inches from the end of the sample. The burn rate is calculated according to the formula:

$$B = 60 \times (D/T)$$

30

B = burn rate in inches per minute

D = Length the flame travels in inches

T = Time in seconds for the flame to travel D inches

5

Table 1

Raw Materials	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
Montell Adflex KS353 (ethylene propylene copolymer)	100.00	100.00	100.00	100.00	100.00	100.00
Bynel 894 (maleated P.P.)	-	-	-	-	-	-
SCPX (organoclay)	-	-	-	-	-	-
Rheox, EA 2886 (Organoclay)	11.00	-	-	-	-	-
Rheox E-2827 (Organoclay)	-	5.50	5.50	5.25	11.00	5.25
Cloisite 15A (Organoclay)	-	-	-	-	-	-
Cloisite 20 A (Organoclay)	-	-	-	-	-	-
Antioxidant, Irganox 1010	-	0.60	0.60	-	-	-
Stearic Acid	-	-	-	-	-	-
UV Stabilizer, Chimassorb 944FD	-	0.60	0.60	-	-	-
Ferro white CI88063 (Pigment)	-	7.00	7.00	-	-	-
72390 TiO ₂	-	-	-	-	-	17.50
Hydraprint aluminum silicate	-	5.50	-	-	-	-
Micral 9400 (ATH) (flame retardant)	-	-	-	-	-	-

Table 1 Continued

Raw Materials	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12
Montell Adflex KS353 (ethylene propylene copolymer)	100.00	100	100	100	100	100
Bynel 894 (maleated P.P.)	-	-	-	-	-	-
SCPX (organoclay)	-	-	-	-	-	-
RHEOX, EA 2886 (Organoclay)	-	5.5	-	-	-	-
Rheox E-2827 (Organoclay)	6.67	-	-	5.5	5.5	5.5
Rheox EA 108	-	-	-	-	-	-
Rheox EA 2885	-	-	5.5	-	-	-
Cloisite 15A (Organoclay)	-	-	-	-	-	-
Cloisite 20A (Organoclay)	-	-	-	-	-	-
Antioxidant, Irganox 1010	-	0.6	0.6	0.6	0.6	0.6
Stearic Acid	-	-	-	-	-	-
UV Stabilizer, Chimassorb 944FD	-	0.6	0.6	0.6	0.6	0.6
Ferro white C188063 (Pigment)	-	7	7	7	7	7
72390 TiO ₂	-	-	-	-	-	-
Hydraprint aluminum silicate	13.00	-	-	-	5.5	-
Micral 9400 (ATH) (flame retardant)	-	20	20	20	-	-

Table 1 Continued

Raw Materials	Example 13	Example 14	Example 15	Example 16	Example 17	Example 18
Montell Adflex KS353 (ethylene propylene copolymer)	100	100	100	100	100	100
Bynel 894 (maleated P.P.)	-	-	-	-	-	-
SCPX (organoclay)	-	-	-	-	-	-
RHEOX, EA 2886 (Organoclay)	-	-	-	-	-	-
Rheox E-2827 (Organoclay)	5.5	8	-	-	-	-
Cloisite 15A (Organoclay)	-	-	8	-	-	-
Cloisite 20 A (Organoclay)	-	-	-	8	-	-
Antioxidant, Irganox 1010	0.6	0.75	0.75	0.75	0.6	0.6
Stearic Acid	-	0.05	0	0	-	-
UV Stabilizer, Chimassorb 944FD	0.6	0.75	0.75	0.75	0.6	0.6
Ferro white C188063 (Pigment)	10	12	15	15	7	7
72390 TiO ₂	-	-	-	-	-	-
Hydraprint aluminum silicate	-	-	-	-	5.5	5.5
Micral 9400 (ATH) (flame retardant)	20	-	-	-	-	20

Table 1 Continued

Raw Materials	Example 19	Example 20	Example 21	Example 22	Example 23	Example 24
Montell Adflex KS353 (ethylene propylene copolymer)	100	100	100	100	100	100
Bynel 894 (maleated P.P.)	3.7	3.7	3.7	3.7	3.7	3.7
SCPX (organoclay)	-	-	12	-	-	12
RHEOX, EA 2886 (Organoclay)	-	-	-	-	-	-
Rheox E-2827 (Organoclay)	-	-	-	-	-	-
Cloisite 15A (Organoclay)	-	12	-	-	12	-
Cloisite 20 A (Organoclay)	12	-	-	12	-	-
Antioxidant, Irganox 1010	0.7	0.7	0.7	-	-	-
Stearic Acid	-	-	-	-	-	-
UV Stabilizer, Chimassorb 944FD	0.7	0.7	0.7	-	-	-
Ferro white CI88063 (Pigment)	7	7	7	-	-	-
72390 TiO ₂	-	-	-	-	-	-
Hydraprint aluminum silicate	-	-	-	-	-	-
Micral 9400 (ATH) (flame retardant)	-	-	-	-	-	-

RESULTS**Table 2**

Sample No.	1	2	3	4	5	6	7	8	9
MVSS-302 TEST RESULTS	2.22	2.24	2.02	3.13	2.22	3.14	2.53	2.42	2.81

Sample No.	10	11	12	13	14	15	16	17	18
MVSS-302 TEST RESULTS	2.68	2.24	2.02	2.44	1.75	2.97	Self Exting- uished	6.26	6.42

Sample No.	19	20	21	22	23	24
MVSS-302 TEST RESULTS	4.09	2.26	2.35	4.06	2.29	2.17

As can be seen from the formulations listed in Table 1 and the results listed in Table 2, the compositions of the present invention exhibit greatly enhanced flame retardant properties as compared to a typical polyolefin formulation. The results also show that typical polyolefin formulations do not pass the MVSS-302 burn test, and oppositely, compositions of the present invention obtain excellent test results.

CLAIMS

What is claimed is:

- 5 1. A flame retardant sheet comprising:
- at least one polyolefin polymer or copolymer or combinations thereof containing repeat units derived from an olefin;
- at least one organically modified clay; and
- optionally, at least one inorganic flame retardant.
- 10
2. A flame retardant sheet according to claim 1, wherein the amount of said inorganic flame retardant is from about 0.1 to about 50 parts by weight per 100 parts by weight of said polyolefin polymer or copolymer or combinations thereof, and wherein said
- 15 sheet has a burn rate of about less than 4 inches per minute according to test MVSS-302.
3. A flame retardant sheet according to claim 2, wherein said sheet is substantially free of polar organic and halogenated organic flame
- 20 retardants.
4. A flame retardant sheet according to claim 3, wherein said polyolefin polymer or copolymer is polyethylene, polypropylene, maleated polypropylene, ethylene-vinyl acetate copolymer,
- 25 ethylene-propylene rubber, or ethylene-octene copolymer, or combinations thereof, and wherein the amount of said organically modified clay is from about 2 to about 20 parts by weight based on 100 parts by weight of said polyolefin polymer or copolymer or combinations thereof.

5. A flame retardant sheet according to claim 4, wherein the amount of said organically modified clay is from about 3 to about 15 parts by weight, wherein said organically modified clay has a particle size of from about 100 to about 2,000 nanometers and forms a nanocomposite with said polyolefin polymer copolymer, and wherein said polyolefin polymer or copolymer is said ethylene-propylene rubber, or said maleated polypropylene, or said ethylene-octene copolymer, or combinations thereof.
6. A flame retardant sheet according to claim 5, wherein the amount of said inorganic flame retardant is from about 15 to about 30 parts by weight.
7. A flame retardant sheet according to claim 6, wherein said organically modified clay is derived from a cation exchangeable smectite clay which has a cation exchange capacity of at least 75 milliequivalents per 100 grams of clay.
8. A flame retardant polyolefin composition, comprising:
at least one polyolefin polymer or copolymer or combinations thereof having from 2 to about 8 carbon atoms per repeat group; an organically modified clay; and optionally at least one inorganic flame retardant; and
wherein said polyolefin and said clay are in the form of a nanocomposite.
9. A flame retardant polyolefin composition according to claim 8, wherein said inorganic flame retardant is present in an amount from about 0.1 to about 50 parts by weight per 100 parts by weight of said polyolefin polymer or copolymer or combinations

thereof, and wherein said composition has a burn rate of about less than four inches per minute according to test MVSS-302.

- 5 10. A flame retardant polyolefin composition according to claim 9,
 wherein said composition is substantially free of polar organic
 and halogenated organic flame retardants.
- 10 11. A flame retardant polyolefin composition according to claim 10,
 wherein said composition has a burn rate of about less than three
 inches per minute according to test MVSS-302.
- 15 12. A flame retardant polyolefin composition according to claim 11,
 wherein said polyolefin polymer or copolymer is polyethylene,
 polypropylene, maleated polypropylene, ethylene-vinyl acetate
 copolymer, ethylene-propylene rubber, ethylene-octene
 copolymer, or combinations thereof, and wherein the amount of
 said organically modified clay is from about 2 to about 20 parts
 by weight based on 100 parts by weight of said polyolefin
 polymer or copolymer or combinations thereof.
- 20 13. A flame retardant polyolefin composition according to claim 12,
 wherein the amount of said organically modified clay is from
 about 3 to about 15 parts by weight, and wherein said polymer
 or copolymer is said ethylene-propylene rubber, or said maleated
25 polypropylene, or said ethylene-octene copolymer, or
 combinations thereof.
- 30 14. A flame retardant polyolefin composition according to claim 13,
 wherein the amount of said inorganic flame retardant is from
 about 15 to about 30 parts by weight; and wherein said

organically modified clay has a particle size of from about 200 to about 1,000 nanometers.

5 15. A flame retardant polyolefin composition according to claim 14, wherein said organically modified clay is derived from a cation exchangeable smectite clay which has a cation exchange capacity of at least 75 miliequivalents per 100 grams of clay.

10 16. A flame retardant laminate, comprising:
a reinforcing layer;
a polymer layer; and
a flame retardant nanocomposite layer comprising at least one polyolefin polymer or copolymer or combinations thereof having from 2 to about 8 carbons per repeat
15 group; at least one organically modified clay; and optionally, at least one inorganic flame retardant.

20 17. A flame retardant laminate according to claim 16, wherein said inorganic flame retardant is present in said nanocomposite layer in an amount from about 0.1 to about 50 parts by weight per 100 parts by weight of said polyolefin polymer or copolymer or combinations thereof, and wherein said nanocomposite layer has a burn rate of about less than four inches per minute according to test MVSS-302.

25 18. A flame retardant laminate according to claim 17, wherein said nanocomposite layer is substantially free of polar organic and halogenated organic flame retardants, and wherein said reinforcing layer comprises a polymer fabric reinforcing layer.
30

19. A flame retardant laminate according to claim 18, wherein said polyolefin polymer or copolymer of said flame retardant nanocomposite layer is polyethylene, polypropylene, maleated polypropylene, ethyl-vinyl acetate copolymer, ethylene-propylene rubber, or ethylene-octene copolymer, or combinations thereof, and wherein the amount of said organically modified clay is from about 2 to about 20 parts by weight based on 100 parts by weight of said polyolefin polymer or copolymer or combinations thereof.
20. A flame retardant laminate according to claim 19, wherein said nanocomposite layer has a burn rate of about less than three inches per minute according to test MVSS-302.
21. A flame retardant laminate according to claim 20, wherein said polyolefin polymer or copolymer of said nanocomposite layer is said ethylene-propylene rubber, or said maleated polypropylene, or said ethylene-octene copolymer, or combinations thereof, wherein the amount of said organically modified clay is from about 3 to about 15 parts by weight, and wherein said polymer fabric reinforcing layer is located between said polymer layer and said flame retardant nanocomposite layer.
22. A flame retardant laminate according to claim 21, wherein the amount of said inorganic flame retardant of said nanocomposite layer is from about 15 to about 30 parts by weight, wherein said polymer fabric reinforcing layer is a woven or non-woven polymer fabric layer, and wherein said polymer layer is a polyolefin polymer or a copolymer or combinations thereof, or a polyvinyl chloride layer.

23. A flame retardant laminate according to claim 22, wherein said organically modified clay of said nanocomposite layer is derived from a cation exchangeable smectite clay which has a cation exchange capacity of at least 75 miliequivalents per 100 grams of clay.
24. A method for preparing a flame retardant composition comprising the steps of:
- mixing and forming a flame retardant nanocomposite comprising:
 - at least one polyolefin polymer or copolymer or combinations thereof having from 2 to about 8 carbon atoms per repeat group;
 - an organically modified clay; and
 - optionally at least one inorganic flame retardant.
25. A method for preparing a flame retardant nanocomposite according to claim 24, wherein said polyolefin polymer or copolymer is polyethylene, polypropylene, maleated polypropylene, ethylene-vinyl acetate copolymer, or ethylene-octene copolymer, or ethylene-propylene rubber, or combinations thereof, wherein the amount of said organically modified clay is from about 2 to about 20 parts by weight based on 100 parts by weight of said polyolefin polymer or copolymer or combinations thereof, and wherein said composition has a burn rate of about less than four inches per minute according to test MVSS-302.
26. A method for preparing a flame retardant sheet according to claim 25, wherein said inorganic flame retardant is present in an

5 amount from about 0.1 to about 50 parts by weight per 100 parts by weight of said polyolefin polymer or copolymer or combinations thereof, and wherein said composition is substantially free of polar organic and halogenated organic flame retardants, and wherein polyolefin polymer or copolymer is said ethylene-propylene rubber, or said maleated polypropylene, or said ethylene-octene copolymer, or combinations thereof.

10 27. A method for preparing a flame retardant nanocomposite according to claim 26, wherein said organically modified clay is derived from a cation exchangeable smectite clay which has a cation exchange capacity of at least 75 miliequivalents per 100 grams of clay.

15 28. A method according to claim 24, including forming said nanocomposite into a sheet.

20 29. A method according to claim 26, including forming said nanocomposite into a sheet.

30 30. A method according to claim 28, including forming said nanocomposite sheet into a laminate.

25 31. A method according to claim 29, including forming said nanocomposite sheet into a laminate.

INTERNATIONAL SEARCH REPORT

Inte Application No

PCT/US 01/02278

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08K3/34 C08K9/04 B32B27/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08K C08L B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 13, 30 November 1999 (1999-11-30) -& JP 11 228748 A (SEKISUI CHEM CO LTD), 24 August 1999 (1999-08-24) abstract	1-15, 24-29
Y	---	2-7, 9-15, 17-23, 26, 27, 30, 31
	--- -/-	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

9 May 2001

Date of mailing of the international search report

16/05/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Russell, G

INTERNATIONAL SEARCH REPORT

Inter. Classification No.

PCT/US 01/02278

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 114 174 A (BERK LTD) 15 May 1968 (1968-05-15) page 2, line 35 - line 41; examples 1-23 claims	1-15, 24-29
Y		2-7, 9-15, 17-23, 26,27, 30,31
X	WO 99 01504 A (TETRA LAVAL HOLDINGS & FINANCE ;FRISK PETER (US)) 14 January 1999 (1999-01-14) example 1 claims 1-5,10,13,18,19 figures 2B,3B,4B,5B,6B	1,8,16, 24,25, 28-31
Y		2-7, 9-15, 17-23, 26,27
X	US 3 506 477 A (DESAULNIERS CHARLES W ET AL) 14 April 1970 (1970-04-14) column 17, line 55 - line 56 claims 7-18	1,8,16, 24,25, 28-31
Y		2-7, 9-15, 17-23, 26,27
P,X	WO 00 68312 A (BEYER GUENTER ;EUPEN KABELWERK (BE); ENGELHARDT THOMAS (DE); SIMML) 16 November 2000 (2000-11-16) the whole document	1-15, 24-29
P,X	WO 00 66657 A (ALCAN INT LTD ;DAVID MARIE L (FR); BROWN STEPHEN C (GB); EVANS KEN) 9 November 2000 (2000-11-09) page 5, line 6 example 1 claims 1-4,6,7,9,12-15	1-15, 24-29
P,X	EP 0 995 591 A (SHOWA DENKO KK) 26 April 2000 (2000-04-26) examples 1-11 claim 4	1,3,5-8, 16,24-31

INTERNATIONAL SEARCH REPORT

Inform  patent family members

Inter  cation No
PCT/US /02278

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 11228748 A	24-08-1999	NONE	
GB 1114174 A	15-05-1968	DE 1544666 A US 3516959 A	10-04-1969 23-06-1970
WO 9901504 A	14-01-1999	US 6117541 A AU 7978998 A EP 0994913 A	12-09-2000 25-01-1999 26-04-2000
US 3506477 A	14-04-1970	NONE	
WO 0068312 A	16-11-2000	DE 19921472 A	16-11-2000
WO 0066657 A	09-11-2000	AU 4422400 A	17-11-2000
EP 0995591 A	26-04-2000	JP 2000129056 A	09-05-2000

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.